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TRANSLATION

PROPERTIES AND USES OF RHENIUM

By

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FOREIGN TECHNOLOGY DIVISION

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PROPERTIES AND USES OF RHENIUM

by

K. B. Povarova and M. A. Tylkina

Rhenium is a rare scattered metal which possesses unique physico-chemical properties which enable one to use it in nuclear-power engineering, electrical technology and electronics. This metal has high qualities when dealing with high temperatures and stresses, and this is of great significance in modern technology of high velocities, temperatures and pressures.

Rhenium is arousing much interest both in the USSR and in a number of foreign countries (U.S.A., France, England, Poland, West German Republic and others). Only in the last four years on the problem of rhenium there have been held four huge conferences -- in 1958 in Moscow, in 1960 in Chicago and in 1962 in Moscow*.

The searches for especially heat-resistant alloys naturally compels one to turn to the metals that are the most difficult to fuse, particularly, particularly to rhenium and its alloys with the metals of the so-called "big four", tungsten, tantalum, molybdenum and niobium.

The double and triple alloys with tungsten and molybdenum, containing 25 to 35 at. % (atomic percent) of rhenium are highly plastic and possess better indices for processing, industrial usability and welding adaptability than unalloyed tungsten and molybdenum. The temperature of their recrystallization is higher by 300 to 500°.

Some of these alloys (molybdenum - 35 at. % of rhenium) can be processed cold with a degree of reduction of more than 90% without intermediate tempering. Both at room temperature and at high temperature these alloys possess high strength (for alloys of tungsten with 25 to 30% of rhenium 30 to 44 kG/mm² at 1500°C and 14 to 16 kG/mm² at 1800°C). The temperature of the transition from the plastic state to the brittle is very much lowered and is around - 200°C for molybdenum-rhenium alloys

*The Proceedings of the first two conferences were published in compendiums: Rhenium, Publishing Office of the Academy of Sciences of the USSR, 1961; Rhenium, Amsterdam-New York, 1962.

and 50 to 120°C for tungsten-rhenium alloys. All these properties justify one's considering alloys of rhenium with tungsten and molybdenum as having the best prospects and being the most promising heat-resistant construction materials for working with temperatures of 1800 to 2000°C.

Significant interest is afforded by the application of small additions of rhenium for alloying nickel-chromium alloys, the temperature of recrystallization of which in this is raised by 200 to 250°C, and the time to breakdown in tensile-strength tests at 800 to 1000°C is lengthened by a factor of ten.

It is known that welded joints of molybdenum at room temperature are brittle and welding of tungsten as yet has not been mastered. The welded unions of the alloys of molybdenum and rhenium produced in a medium of argon and an electron beam withstand a bending test to an angle of 180° with a radius of the bend equal to three thicknesses of the plate, and also submit to cold deformation by rolling with a degree of reduction of 70% without the formation of any cracks in the joint or the region around the joint.

With electron-beam welding of double alloys of rhenium and tungsten one attains a plasticity of the seam which is characterized by an angle of bending up to 33°. With the welding of the triple tungsten-molybdenum-rhenium alloy one gets an angle of 180°. A considerable effect is obtained by the use of rhenium or its alloys with molybdenum as the welding material for the welding of molybdenum.

There are good prospects for the use of alloys of rhenium in electrical-instrument making inasmuch as rhenium and some of its alloys possess high elastic properties. Thus the introduction of rhenium into cobalt alloys made it possible to solve the problem of improving the hardness and resistance to abrasion and assured the dependability of the cores of electrical instruments under conditions of vibration and increased loads.

The potentiometric alloys of rhenium and the precious metals possess high specific electrical resistance and low-temperature coefficient of electrical

resistance.

The alloys of rhenium and tungsten are used for high temperature thermo-couples for the purpose of precise measurement and constant control of temperature above 2000 to 2500°C.

Up until recent times for the measurement of such temperature optical pyrometers were used, and for more precise but brief periodical measurements of temperature, thermo-couples of the platinum group (up to 1800°C) or tungsten-molybdenum thermo-couples (2000°C) which, after being used at high temperatures took on a brittleness and instability of the thermoelectric properties.

With the use of tungsten-rhenium thermo-couples of the type W—5% RE/W—20% Re and others these shortcomings are eliminated. Such thermo-couples possess high thermo-electromotive force (up to 2900°C). They have a high melting temperature (above 3000°C), stability at high temperatures in a protecting medium (hydrogen, inert gas, vacuum). and also a relatively low vapor pressure of the component.

Besides this, they possess considerably higher mechanical properties, and do not become brittle after being used at high temperatures. At the present time thermo-couples of such a type are widely used both in the USSR and abroad for the measurement of temperature above 2000°C.

For the dependable working of electrical instruments there are necessary contact materials with low contact resistance (which is usually characteristic of low melting metals with little hardness) and with a low factor of erosion in arc operation (something found in hard, strong materials which have a high melting point and boiling point).

Of the metals with a high melting point most often one takes for the contacts tungsten and molybdenum. However, these metals are subject to corrosion, and on them are formed oxide films, which lead to the breakdown of the contact.

Rhenium and its alloys with metals with a high-melting point (with tungsten) can be used as a splendid contact material. The transition resistance of such

contacts, as distinguished from the contacts made of tungsten, changes little with the course of time, and also with working under conditions of high temperatures. After 10,000 operations in the arc system, the transition resistance of tungsten increases 20 times as much as that of rhenium.

It is very important that the rhenium contacts can be successfully used under the conditions of atmospheric, tropical and marine corrosion, while tungsten contacts get completely out of order within two days.

Due to the good working characteristics in electrical tests and the high corrosion strength, it is to advantage to use the rhenium contacts in a magneto of average power for suspension motors which work under conditions of great moisture, in relays which work with voltages of about 6 v, current of 1 to 1.4 amp, and number of operation $8.5 \cdot 10^6$ 1 hr, and also in automatic relays in hermetically isolated systems of reactive combustion.

Of great significance is the use of rhenium in electronics. When using it as a thermocathode, i. e., with the selecting of small currents, rhenium has a number of advantages over tungsten, since it is less subjected to cathode atomizing and adsorption of residual gases, and in distinction from other high-melting metals, does not form carbides.

Rhenium or rheniumized cathodes can be used as auto-emission cathodes, for example, in ionization manometers or the irradiation units of mass spectrometers. It is very advantageous also to use uranium for the core of high-temperature oxide cathodes for which nickel is no longer suitable in working in the system of joint taking off of the flow of thermal and secondary electron emission in instruments of the magnetron type.

In the use of oxide thorium-itrrium, thorium-lanthanum and itrrium-lanthanum coatings which possess a high coefficient of secondary emission on a rhenium core, it is possible to create good emitters for vibration-resistant instruments and powerful generator tubes.

The use of rhenium and its alloys with tungsten and molybdenum, as a construction element in electro-vacuum instruments, is determined by a number of factors, among them a little role being played by the fact that rhenium, contrary to tungsten, will not enter the "hydraulic cycle".

In connection with the fact that the rate of vaporization of rhenium in the presence of water vapor is several times less than that of tungsten, much popularity at the present time has been given to heating elements made of rhenium and tungsten-rhenium and molybdenum-rhenium alloys. This led to a considerable increase in the period of service of the elements, in particular in reception-amplifying tubes.

There is information to the effect that in the U.S.A. from rhenium and its alloys there are being made parts which operate at high temperatures (grids of klystrons, anodes of generator tubes, etc.).

The great resistance of rhenium in ion bombarding is of great significance also in a number of instruments.

For protection of the parts from ion bombardment, the action of the "hydraulic cycle" and carbon ones uses rheniumizing of tungsten control grids of radio tubes, molybdenum spiral tubes of traveling waves, copper units of magnetrons and some other parts.

It is known, in particular, about the use of alloys of rhenium with tungsten in X-ray diagnosis tubes (FRG) in which formerly there was used a revolving tungsten anticathode making it possible to obtain high power with little focus. However, in this the track heated up by the electrons creates along the section of the anticathode a gradient of some thousands of degrees per 1 mm but the recalcination of the surface leads to a weakening of the intensity of the X-ray radiation in the process of the work.

Simmons Company (FRG) used in the anticathodes a surface layer of the alloys of tungsten with 5 to 10% of rhenium. Such anticathodes lose only 11 to 20% of their original intensity of radiation after being turned on 10,000 times, whereas

the formerly used tungsten anticathodes lost 50%. As a result there was attained an increase in the power and the service life of the X-ray tube.

In this way the use of rhenium and its alloys and coatings of them as materials for metallic thermocathodes, pores of thermocathodes, automatic electron emitters, heaters, and parts of instruments that are strong and resistant against outside action proves to be a new step in the development of vacuum electronics.

As is known, rhenium is a superconductor. It passes into the superconductor state at 1.699°K. A number of alloys of rhenium with transitional metals, in particular, many compounds of rhenium with a structure of the type σ or χ , phase (α -- Mn) also possess superconducting properties while the temperature of transition into the superconducting state stands at 9 to 11°K.

In the U.S.A. use was found for the alloy of molybdenum with 25 at. % of rhenium, from which there was made a solenoid for work in fields of more than 15 kgauss at low temperatures (about 4.2°K).

Two compounds of rhenium, dicilicide and diselenide, turn out to be semi-conductors. However, it is too soon to talk about their practical use.

The catalytic properties of rhenium are very valuable. Pure rhenium and a mixed copper-rhenium catalyst are capable of effecting hydrogenation of CO in methane with an admixture of ethane and ethylene in the ethane. The rhenium catalyst not only does not lose its activity on scouring by H_2S or As_2O_3 but even increases it. With the application of metallic rhenium onto activated carbon, one gets active catalysts of the dehydration of organic compounds.

The use of rhenium catalysts instead of the earlier used ones for the dehydration of cyclic hydrocarbons enabled one to increase substantially the speed of the process and reduce the energy of the activation. The active rhenium catalysts enable one to effect dehydration of spirits at low temperature with a high yield.

Rhenium possesses high corrosion resistance as against different corrosive agents (such as sulfuric and chloric acids, alkali, liquid gallium, etc.), as a

result of which it is of great interest for the chemical and the electro-vacuum industries, electrical technology and other lines. However, in cases where the basic significance is had by the surface properties of a part it is advantageous not to make the part out of rhenium or its alloys but limit oneself to the respective coating.

The basic methods of the application of coatings are electrolytic or from the gas phase (halide and carbonyl).

The list of possible areas for using rhenium is not exhausted, since the physico-chemical properties of rhenium and its alloys have not yet been sufficiently studied. However, it is already quite clear that rhenium is a very promising metal for use in a number of branches of technology, and in certain cases it is absolutely not replaceable. At the same time on account of the shortage of rhenium and its alloys it must be used for the making of parts of small dimensions only in unique constructions, and also in those cases where, because of the aggregate of properties no other metal can be used.